Figure 57 shows a frequency distribution of the test days that the percentage of sulfur in the lignite emitted as $SO_2$ (referred to as S.E.) was in a given range. Results are shown separately for each method of firing. In 29 of the 39 test days with pc firing, S.E. was in the range of 60 to 90 pct. The minimum value was 48 pct, and the maximum was 100 pct. Some of the reasons for these variations will be discussed later.

With cyclone firing, S.E. was in the 80- to 100-pct range for 4 days and in the 70- to 80-pct range for 1 day. One would expect less retention of the sulfur with the ash in a cyclone furnace because of the smaller percentage of ash that is carried through the boiler as fly ash. That portion of the ash that is melted into slag contains very little sulfur.

Two test days were on a spreader-stoker-fired plant. In one test, S.E. was 29 pct, and in the other, 42 pct. The lignites burned during these tests were very low in sulfur, 0.59 and 0.56 pct on a dry basis, and the ash had high sodium oxide contents of 10.9 and 8.6 pct. These factors combined to produce the very low emission rates, which cannot be assumed to be typical for spreader-stoker-firing. The grate ash from a spreader-stoker unit should not retain much sulfur and the percentage of ash carried over is less than for pc firing, so less sulfur retention would be expected.

## Prediction of $SO_2$ Emissions

The retention of sulfur in lignite fly ash is due to the presence of alkali constituents such as calcium, magnesium, sodium, and potassium in reactive form. Calcium and sodium sulfates have been identified in significant concentrations in lignite fly ash by X-ray diffraction. Water-solubility stoichiometric data suggests all soluble sodium and potassium in the fly ashes are present as sulfates, but only a portion of the soluble calcium is as sulfate. The water solubility of magnesium in the fly ash is highly pH sensitive, and sulfate in solution does not increase as magnesium dissolution increases with lowered pH, suggesting there is little $MgSO_4$ in a typical lignite fly ash. Since potassium is generally present in lignites in very small amounts, the alkalis most responsible for $SO_2$ retention in lignite fly ash are calcium and sodium.

Not all calcium and sodium is available for reaction with $SO_2$. Electron microprobe analyses of individual fly ash particles have indicated a significant CaO and $Na_2O$ content in most glassy silicate and aluminum silicate particles appearing in lignite fly ash. These particles result from intimate contact of very fine silica and clay with organically bound calcium and sodium in burning coal particles. This type of particle accounts for the significant fraction of calcium and sodium, which remains insoluble in water, even in solutions having low pH. It is believed that the alkali appearing in these insoluble glassy particles is not reactive towards $SO_2$. Thus silica and clay inherent in the ash could be expected to reduce the fraction of the ash that is active in $SO_2$ pickup.

Field test data from pc-fired units were examined using statistical regression to determine whether correlations existed between ash composition, sulfur content, and the percent sulfur emitted as $SO_2$. The bivariate relationships between individual constituents sodium, calcium, silicon, aluminum, total ash, and sulfur contents in the lignite, and percent sulfur emitted as $SO_2$ are shown in figure 58. The most clearly discernible trends are the increased percent emitted with increased concentrations of $SiO_2$ and $Al_2O_3$ in the coal on a dry basis. Increased sodium and calcium decrease the percent sulfur emitted; however, the correlations are very poor, especially for calcium. No correlation between initial sulfur content and percent emitted is evident. A slight increase in percent of sulfur emitted with increased ash content is indicated, perhaps relatable to increased silica and clay contents in high-ash coals.

Multiple linear regression was employed with more success using the basic model of the form

$$S.E. = C_1 \ (\text{Element A})^W \times (\text{Element B})^X + C_2 \ (\text{Element C})^Y \times (\text{Element D})^Z, \qquad (4)$$

where Elements A, B, C, D, --- were $SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, MgO, $Na_2O$, and S tested in a multiplicity of combinations. Components were expressed as percent of moisture-free lignite. Exponents W, X, Y. Z, --- ranged from -2 to +2 and were tested in a multiplicity of combinations.

The most useful correlation developed for the pc-fired test data combined good predictability and simplicity:

$$S.E. = -12.7 \frac{CaO}{Al_2O_3} - 48.1 \frac{Na_2O}{SiO_2} + 110.1,$$

and

$$\text{and } R^2 = 0.711. \qquad (5)$$

A plot of actual versus predicted percent emission is shown in figure 59.

The $R^2$ indicates 71 pct of the variance in the data is explained by the correlation, a significant improvement over individual predictors. An $R^2$ of 100 pct would indicate perfect agreement between the data and the equation.

The effect of each variable on S.E. can be illustrated by considering the change in S.E. with a 1-pct increase in each ash component on a dry coal basis. This would be roughly equivalent to a 10-pct increase on a percent-of-ash basis. A 1-pct increase in $Na_2O$ (dry coal basis) or a 10-pct increase in the ash would cause a decrease of 20 pct in S.E. A 1-pct increase in CaO would cause a 10-pct decrease in S.E., a 1-pct increase in $SiO_2$ would cause a 6-pct increase in S.E., and a 1-pct increase in $Al_2O_3$ would cause a 10-pct increase in S.E. It should be noted that in other regression relations developed, the effect of sodium relative to calcium may be increased to a 3:1 ratio. The generally greater effect of sodium reflects a higher reactivity toward $SO_2$.

The prediction formula confirms quantitatively that alkalis are responsible for $SO_2$ removal, and silicates and clays would retard removals by tying up alkalis. The ratio of CaO to $Al_2O_3$ suggests that CaO reacts preferentially

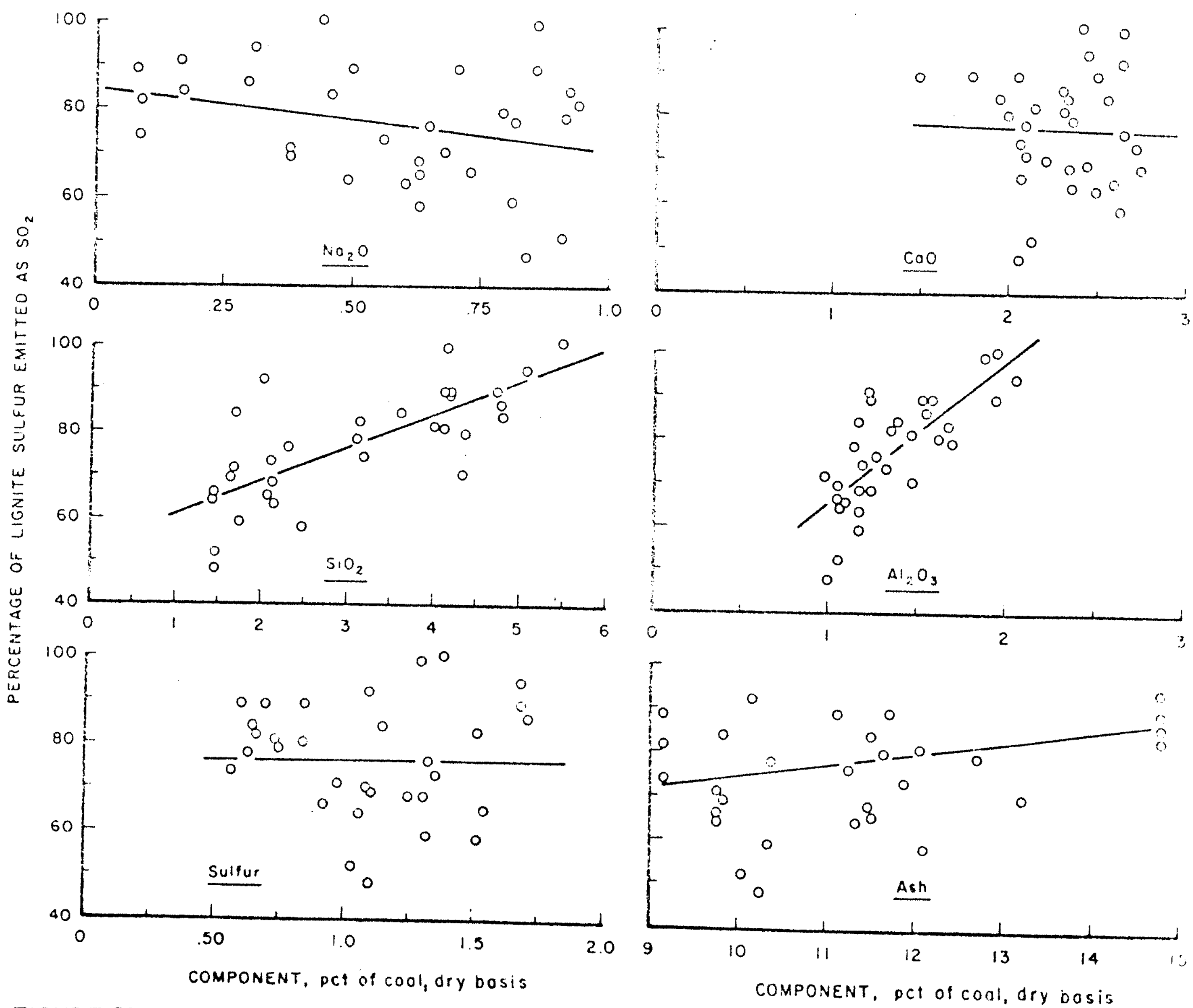



FIGURE 58. - Correlation of lignite and ash analysis with percentage of sulfur emitted for pc-fired units.

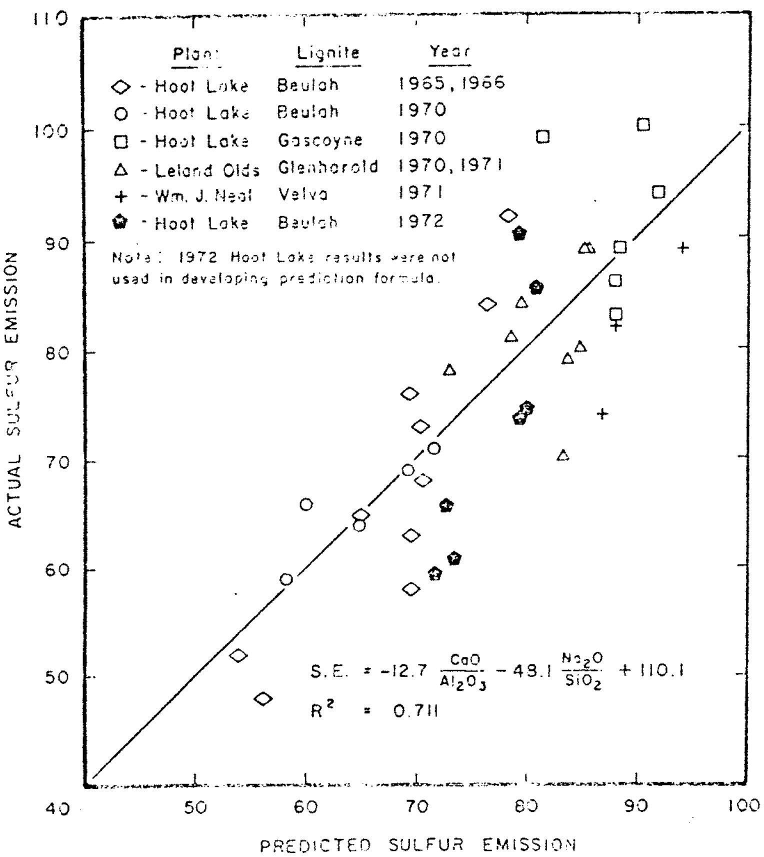



FIGURE 59. - Predicted versus actual sulfur emission (S.E.) for pc-fired plants.

with clay, but $Na_2O$ would react more readily with silica as mechanism for decreasing alkali reactivity.

The fact that the model suggests that S.E. is not a function of sulfur level deserves additional discussion. Sulfur was considered in all possible combinations in the model, but did not increase $R^2$ more than a trivial amount. In the equation for S.E., coal sulfur is a divisor (that is,

$$S.E. \approx \frac{\text{ppm } SO_2 \text{ emitted}}{\text{S in coal}}).$$

If both sides of equation 5 are multiplied by percent S in dry coal, the apparent dilemma is resolved. Then S.E. becomes absolute sulfur emitted, expressed as a function of the product of the alkali clay silica ratio with sulfur. It can then be seen that the model suggests sulfur retention is relatable to a first-order alkali sulfur reaction scheme.

In figure 59, some data not included in the regression are plotted. These are data for 1972 Hoot Lake, Beulah lignite tests. All other points on the plot were used to develop the relationship. The correlation explains data from the Hoot Lake tests as well as those originally included in the regression.

## Effect of Sodium on $SO_2$ Emissions

Sodium has been shown to have the greatest effect on sulfur emitted from lignite-fired boilers. In tests at the Hoot Lake plant in 1972, low- and high-sodium lignites from one mine were tested for succeeding weeks. The sodium content was the only substantial variable in the tests (see analysis in table 7), and any variation can be attributed to changed sodium concentration. The results from 3 test days on each coal is shown in figure 60. The parts per million $SO_2$ decreased from about 800 ppm to about 590 ppm when the sodium was increased from 0.9 to 6.1 pct. A disadvantage of the high sodium content is, of course, an increased ash fouling rate.

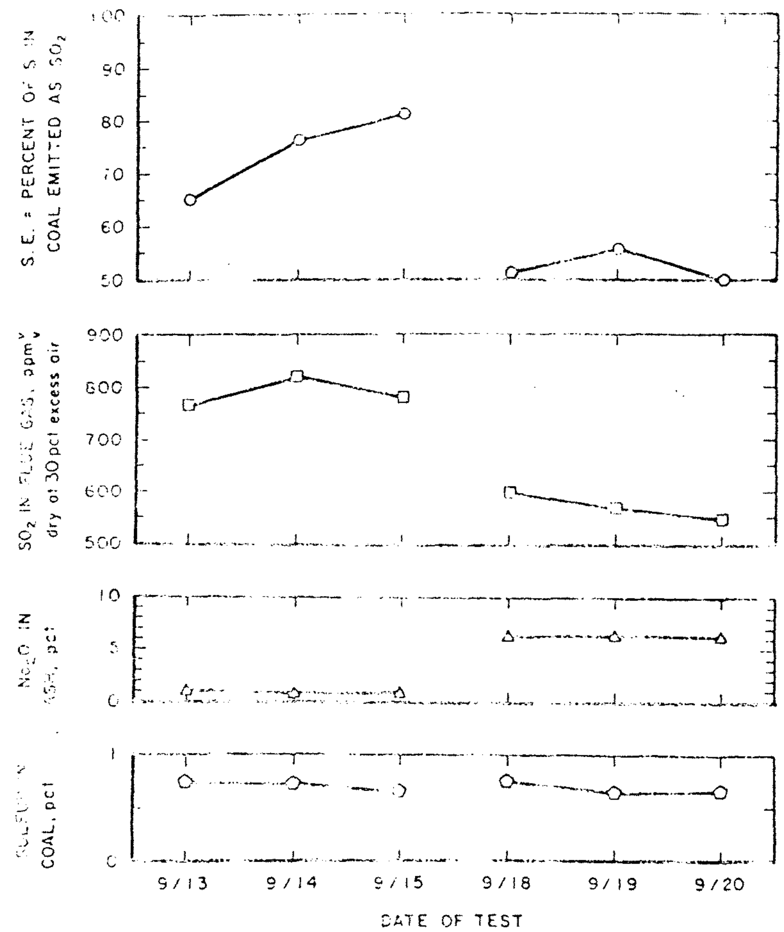



FIGURE 60. - Effect of sodium content in lignite on $SO_2$ emissions, Hoot Lake tests, 1972.

### Effects of Boiler Load on $SO_2$ Emissions

Sulfur balance studies conducted on plants burning German brown coals have shown that the percent of sulfur retained in the ash is greatly influenced by boiler load and gas residence time.[28] Most tests reported in this study were at 85 to 110 pct of rated load as shown in table 7. The one exception is at the Leland Olds plant where load was reduced to 55 pct for 2 test days. The results show no significant change in $SO_2$ emission when compared with the higher load tests.

### Sulfur Retention in Various Ash Fractions

During most of the field tests, samples of ash were collected from various locations in the boiler for chemical and physical analyses. Results of chemical analysis of selected ashes from the various boilers are shown in table 8. Fly ash samples from both the Leland Olds and Hoot Lake plants were collected during special tests in which a pilot electrostatic precipitator was operating on a side stream of flue gas. In both cases, the electrostatic precipitator dust is considerably enriched in $SO_3$ as compared with the cyclone dust collector sample. In tests conducted at the Hoot Lake plant in 1965-66, four sodium levels in the lignite were studied, and fly ash samples aspirated from the flue gas ahead of the air heater in each case. The $SO_3$ contents of aspirated ash ranged from 6.8 pct with the lowest sodium lignite to 28.3 pct with the highest sodium lignite. During the high-sodium tests, considerable ash was being retained in the furnace because of boiler fouling.

[28] Speich, P. Schwefelbilanzuntersuchungen an Braunkohlenkesselanlagen. (Investigations of Sulfur Balance at Lignite-Fired Boiler Plants.) Braunkohle, v. 17, No. 9, September 1965, pp. 364-371.

TABLE 8. - Partial analysis of selected ash samples from field tests of lignite-fired boilers

| | Component in ash, pct | | | |
|---|---|---|---|---|
| | CaO | MgO | $Na_2O$ | $SO_3$ |
| PC-FIRED TESTS | | | | |
| Hoot Lake plant, 8/12/70: | | | | |
| Mechanical dust collector | 28.8 | 9.1 | 4.2 | 4.5 |
| Pilot electrostatic precipitator | 26.4 | 8.9 | 5.3 | 8.7 |
| Leland Olds plant, 8/28/70: | | | | |
| Mechanical dust collector | 19.9 | 6.0 | 6.9 | 2.3 |
| Pilot electrostatic precipitator | 20.1 | 5.8 | 7.9 | 6.0 |
| Hoot Lake plant, 1965-1966: Samples aspirated from boiler exist dust: | | | | |
| Test 1 | 32.9 | 10.3 | 2.3 | 6.8 |
| Test 2 | 28.5 | 8.6 | 7.2 | 11.6 |
| Test 3 | 26.2 | 9.1 | 9.4 | 14.1 |
| Test 4 | 20.1 | 9.3 | 16.3 | 28.3 |
| CYCLONE-FIRED PLANT | | | | |
| Milton R. Young plant, 1970: | | | | |
| Mechanical dust collector | 32.4 | 8.8 | 1.4 | 3.9 |
| Aspirated from gas to dust collector | 31.5 | 8.4 | 1.4 | 6.7 |
| Bottom slag | 31.8 | 9.5 | .3 | .2 |
| SPREADER-STOKER-FIRED PLANT | | | | |
| Franklin P. Wood plant, 1971: | | | | |
| Mechanical dust collector | 23.5 | 6.4 | 11.8 | 2.9 |
| Aspirated from dust collector exit gas | 3.8 | .9 | 30.5 | 38.0 |
| Grate ash | 19.3 | 4.8 | 8.8 | 1.0 |

The results for the cyclone-fired plant again show that the aspirated fly ash from the furnace exit contained considerably more $SO_3$ than the fly ash caught in the mechanical dust collector. The bottom slag had only 0.2 pct $SO_3$.

Tests conducted on a spreader-stoker-fired boiler during operation on high-sodium lignite showed that the dust collector ash had 2.9 pct $SO_3$ but that the aspirated dust at the dust collector outlet had 38.0 pct $SO_3$ and 30.5 pct $Na_2O$. The grate ash had 1.0 pct $SO_3$.

To summarize these data, the results show wide variation in the amount of sulfur retained with the ash, depending upon alkali content and temperature history of the ash. The fine fly ash fractions are most enriched in $SO_3$; however, without ash balance data one cannot determine the quantity of input sulfur retained in the various fractions. Bottom slag from a cyclone and grate ash from a spreader-stoker retain little sulfur.

## Summary of $NO_x$ Results

Figure 61 shows the results of $NO_x$ determinations at the various plants. The daily averages shown have been adjusted to 30 pct excess air for comparative purposes. The levels for the pc-fired plants ranged from about 300 to 520 ppm. For the cyclone-fired plant, the levels ranged from 570 to 690 ppm, significantly higher, as would be expected from the higher combustion temperatures employed. The value of 230 ppm for the spreader-stoker plant is surprisingly low. These values can be compared with a limit of 0.7 lb/MMBtu (about 550 ppm) for bituminous coal-fired boilers as specified by the national emission standards. At the present time, lignite-fired boilers are specifically exempted from an $NO_x$ limit in the national emissions standards.

## Fly Ash Size Distribution

Two of the most important factors affecting design of fly ash control equipment are the fly ash loading and particle size distribution in the flue gas exiting from the boiler. Determination of dust loading was not a major part of these studies, but size distribution was determined on fly ash samples aspirated from boiler exit ducts during some of the tests. Figure 62 shows the Bahco size analysis of fly ash taken from the boiler exit flue gas at a pc-fired, cyclone-fired, and spreader-stoker-fired boiler. The spreader-stoker fly ash was coarsest, having a mass median diameter of 44 µm with

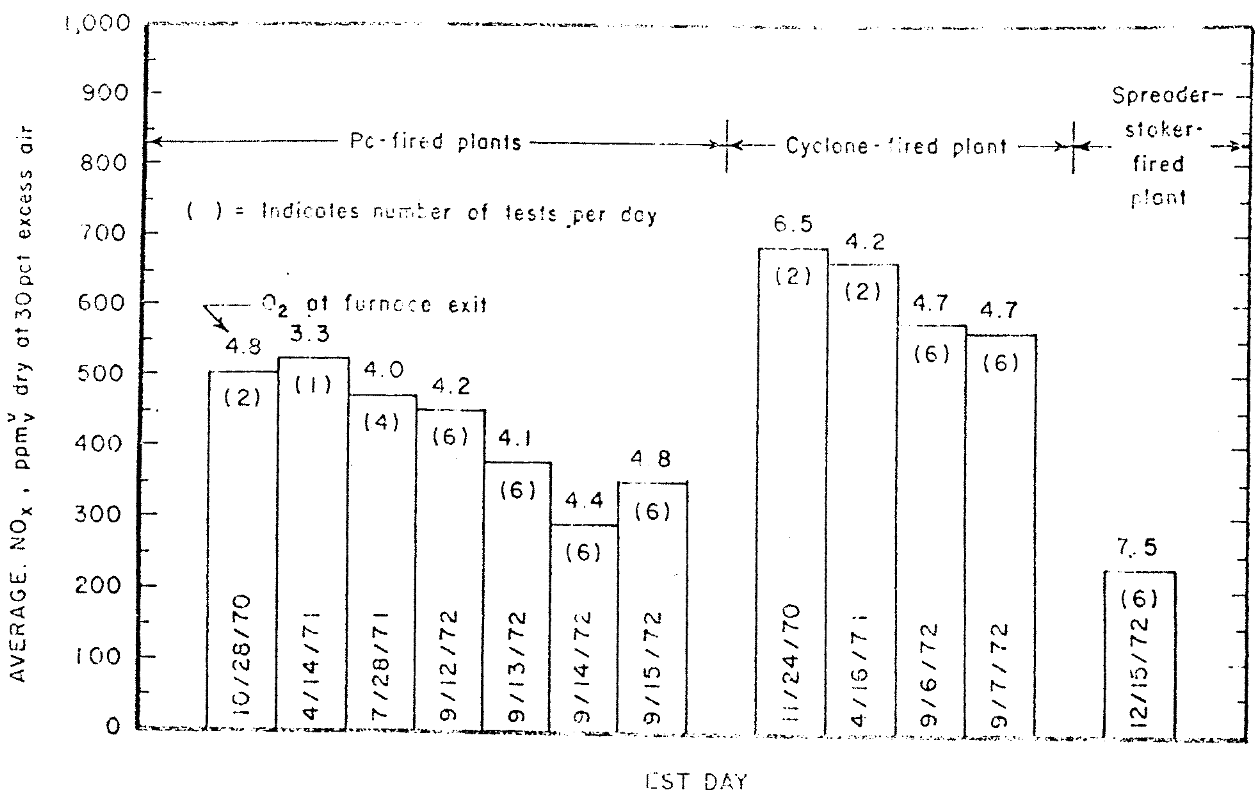



FIGURE 61. - $NO_x$ emissions from various lignite-fired plants. (Boiler loads ranged from 92 to 106 pct of rated capacity.)

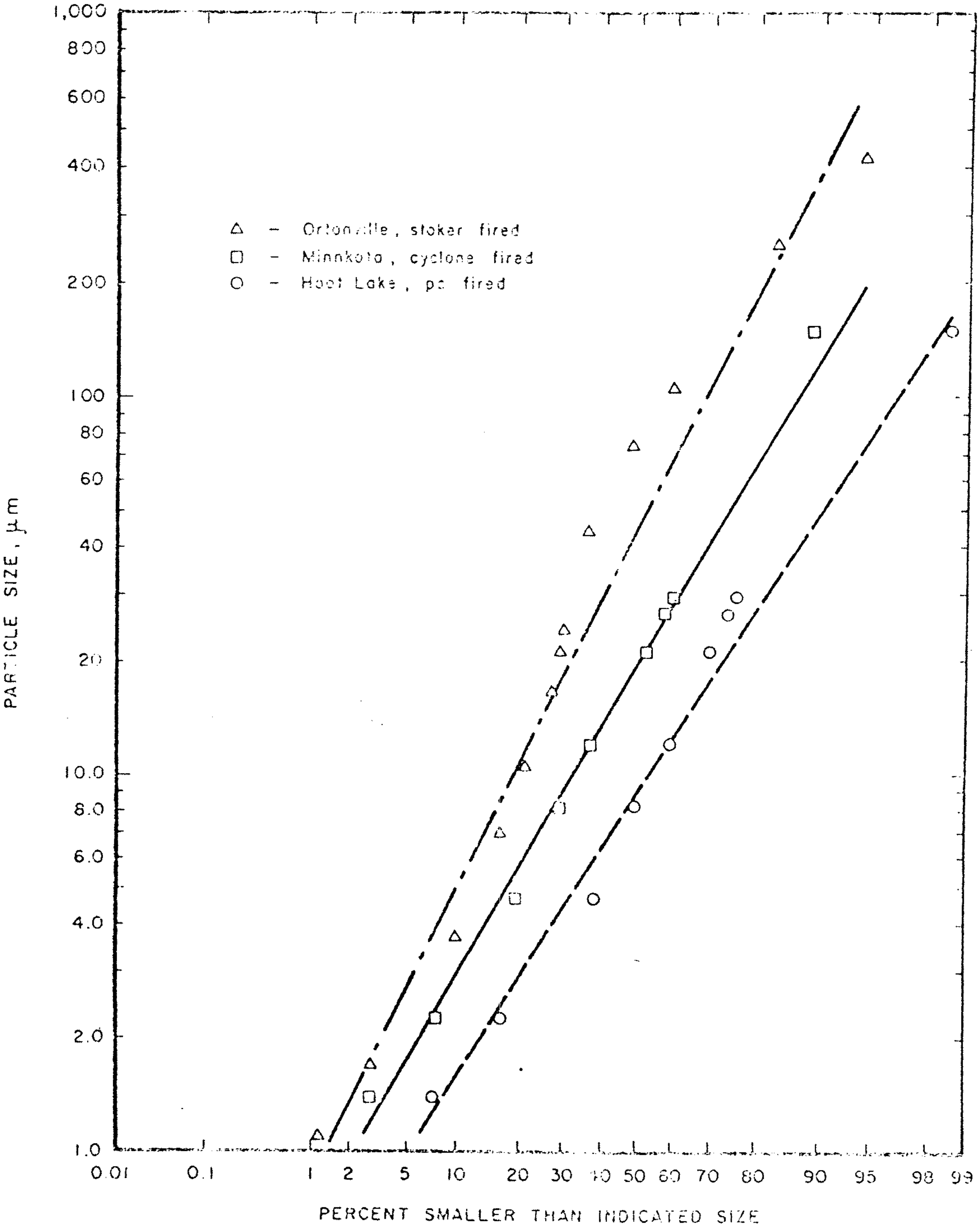
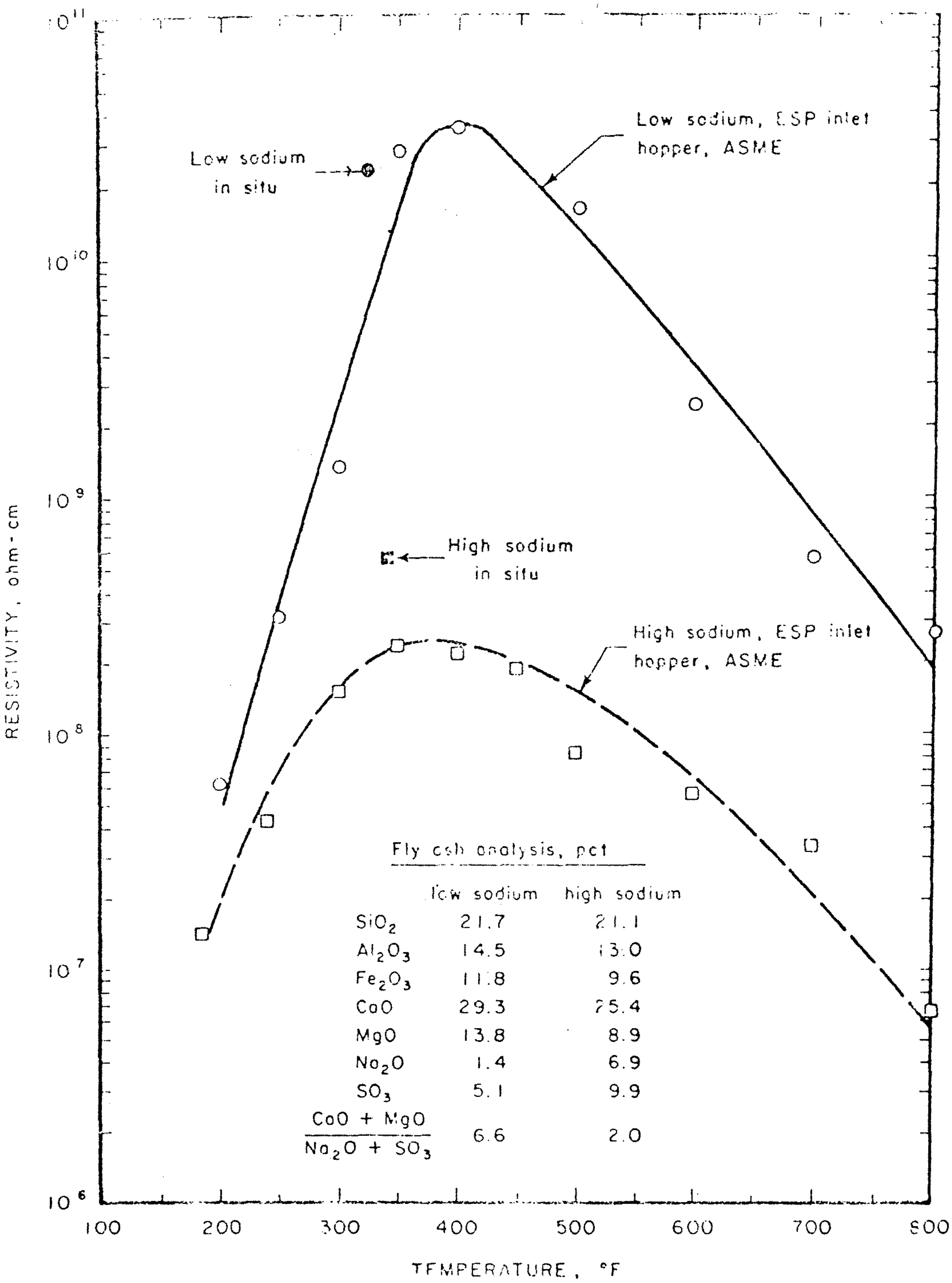



FIGURE 62. - Size analysis (by Bahco method) of fly ash samples aspirated from boiler exit duct.

16 pct below 10 µm. It has been stated in the German literature on brown coal firing that cyclone firing produced a finer fly ash than did pc firing. This was not confirmed by the tests at Milton R. Young and Hoot Lake plants in 1972.




| | low sodium | high sodium |
|---|---|---|
| $SiO_2$ | 21.7 | 21.1 |
| $Al_2O_3$ | 14.5 | 13.0 |
| $Fe_2O_3$ | 11.8 | 9.6 |
| CaO | 29.3 | 25.4 |
| MgO | 13.8 | 8.9 |
| $Na_2O$ | 1.4 | 6.9 |
| $SO_3$ | 5.1 | 9.9 |
| $\frac{CaO + MgO}{Na_2O + SO_3}$ | 6.6 | 2.0 |

FIGURE 63. - Effect of sodium content on electrical resistivity of lignite fly ash.

The mass median size for the cyclone-fired boiler was 18.5 μm with 33 pct below 10 μm and for the pc-fired boiler the mass median size was 7.8 μm with 54 pct below 10 μm. It should be noted that the cyclone-fired boiler was burning a very low sodium coal during these tests, and it is possible that increased volatilization might increase the fine fraction if high alkali lignites were used.

## Electrical Resistivity of Fly Ash

An important factor affecting the electrostatic precipitation of fly ash is the electrical resistivity of the ash. A series of laboratory resistivity tests was run on the fly ash from a number of low-sulfur western coals with the basic data presented previously.[38] A computer study indicated that the ratio $(CaO + MgO)/(Na_2O + SO_3)$ in the fly ash was the best indicator of resistivity for those samples, with resistivity varying directly as the ratio.

In more recent work, the emphasis has been on in situ field resistivity determinations. The effect of sodium in the fly ash is additionally demonstrated by data from the 1972 Hoot Lake tests, shown in figure 63. The low-sodium ash showed a significantly higher (100 X at 350° F) resistivity than did the high-sodium ash for both the laboratory and in situ results. The results also confirm the applicability of the ratio described previously, as the higher resistivity fly ash shows the higher value for $(CaO + MgO)/(Na_2O + SO_3)$. The values determined are within the range for satisfactory precipitator operation despite the low sulfur content of the lignite burned. This is confirmed by the satisfactory performance of the electrostatic precipitator (ESP) units on the Hoot Lake plant since their startup in the spring of 1972.

## Summary and Conclusions

For the past few years, the Bureau of Mines has collected data on stack emissions from various lignite-fired powerplants. Included were tests on pc-fired, cyclone-fired, and spreader-stoker-fired boilers operating on lignites. Most emphasis was on the study of $SO_2$ emissions and how they relate to input sulfur level, firing method, ash analysis, and other factors. Limited data was collected on $NO_x$ emissions from the various plants. Chemical and physical properties of fly ash as a function of firing method were determined, and electrical resistivity studies of the fly ashes were made. A method is given for calculating $SO_2$ and $NO_x$ emission levels and percent of input sulfur emitted as $SO_2$ without knowing the weights of coal burned or flue gas produced.

The principal conclusions are the following:

1. The 1.2-lb/MMBtu $SO_2$ emission limit was exceeded in 33 of the 46 test days. However, with a 40-pct reduction most of the tests would have been under the limit.

[38] Work cited in footnote 23.

2. Significant amounts of sulfur were retained by the ash in most of the tests. The percentage sulfur retained ranged from 0 to 73 pct with most of the results being between 10 and 40 pct.

3. Insufficient data are available to definitely establish a difference in sulfur retention between firing methods, although there are some indications that the retention is less with cyclone firing than with pc firing.

4. The percentage of sulfur retention in ash was not closely reproducible, and some of the variation is probably a result of variability in the input sulfur. Results show the extreme importance of adequate coal sampling if the sulfur balance data is to be meaningful.

5. The $SO_2$ emission is strongly influenced by the sodium content of the coal. Increasing the sodium from 0.9 to 6.1 pct in the ash reduced the $SO_2$ in the combustion gases from 800 to 590 ppm.

6. Sulfur retention in the ash can be predicted from the chemical composition of the ash with some degree of confidence. The computer-derived relationship shows that increasing CaO and $Na_2O$ increases sulfur retention, and clay and silica in the ash tend to decrease sulfur retention.

7. Boiler load does not greatly influence $SO_2$ emissions on the basis of limited testing of a pc-fired unit.

8. $NO_x$ emissions are greater for cyclone-fired than for pc-fired units.

9. The fly ash particle size at the boiler outlet when burning low-sodium-content lignite is greater using cyclone firing than for pc firing.

10. As predicted by a correlation developed in laboratory tests, increasing the sodium content of the ash from 0.9 to 6.1 pct reduced resistivity by a factor of 100 in field tests.